

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Stable Despersible Accelerator Masterbatch for Use in the Vulcanization of Natural or Synthetic Rubber

We, THE GENERAL TIRE & RUBBER COMPANY, a Corporation organized under the Laws of the State of Ohio, United States of America, of 1708 Englewood Avenue, Akron, 5 County of Summit, State of Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of preparing an easily dispersible vulcanizing type of accelerator for use in the vulcanization of natural or synthetic rubber. It relates specifically to substituted thiuram polysulfide compositions.

The desirability of incorporating accelerators of vulcanization into rubber compounds by first preparing a masterbatch of such accelerators (i.e., a rubber mixture containing dispersed therein a higher than normal concentration of accelerator) and then masticating the masterbatch into the desired rubber compound has long been recognized. The use of the masterbatch technique is considered to provide a better degree of dispersion than is readily obtained by the addition of accelerator directly to the final rubber composition. It also prevents a high concentration of accelerator and curing agent from occurring at a given place.

Masterbatches of various accelerators have been made both by the process of latex compounding wherein the accelerator is added to the latex and the coagulum dried and then masticated or masticated and dried, and by the mass compounding process wherein the accelerator is merely mixed by mastication into solid rubber. While masterbatches of most accelerators prepared by either method are suitable for most purposes masterbatches of the class of rubber accelerators known as the substituted thiuram polysulfides when prepared have caused considerable difficulties.

This class of accelerator is both an accelerator and vulcanizing agent. It carries its own sulfur so that when the concentration of accelerator is sufficiently large to provide the acceleration required when the masterbatch or accelerator is to be later added to rubber batches to prepare usable rubber compounds, curing of the rubber in the masterbatch has invariably taken place even at room temperature on standing with the result that the masterbatch itself could not be suitably dispersed in the rubber forming the base for the final usable compound. The alternative was to use the masterbatch quickly.

In accordance with the present invention, a process of making a masterbatch of a curing type of accelerator, comprises mixing a latex of a vulcanizable polymer or copolymer of an conjugated diolefinic compound of less than 8 aliphatic carbon atoms with an aqueous slurry of a solid water-insoluble substituted thiuram polysulfide accelerator, coagulating the mixture thus formed, drying the coagulum while maintaining a temperature below the melting point of said substituted thiuram polysulfide and maintaining said coagulum in an unmasticated condition.

It is thought that solid water-insoluble substituted thiuram polysulfides, when incorporated in accordance with the process of the invention, apparently do not get into vulcanizing contact with rubber particles of the latex coagulum unless the coagulum is either subjected to temperatures above the melting point of the solid substituted thiuram polysulfide accelerator or is subjected to mastication to cause smearing of the accelerator particles into vulcanizing contact with the rubber. Accelerator masterbatches of tetra-methyl-thiuram disulfide, for example, prepared by the above outlined prior methods either by incorporation first with the latex or first in solid rubber by the mastication route, were completely set up and un-

Price 3/-

usable after a month's storage at room temperature, whereas masterbatches prepared in the examples given hereinafter, where neither mastication nor drying at sufficiently elevated temperatures to cause melting of the accelerator was used in their preparation, had, when stored for 18 months, no perceptible set-up and were in excellent condition. Thus, further in accordance with the present invention, a vulcanization accelerator masterbatch for addition to a natural or synthetic rubber during the compounding of the same comprises an unmasticated, unvulcanized polymer or copolymer of a conjugated diolefinic compound of less than 8 aliphatic carbon atoms and at least one water insoluble solid substituted thiuram polysulfide accelerator, said masterbatch being further characterized by being usable as a vulcanization accelerator after a period of storage of at least one month at normal temperatures.

The accelerators suitable for use in the present invention are any of the substituted thiuram polysulfides, including the tetramethyl thiuram disulfide which melts at a temperature of about 146°C. to 148°C.; the dipentamethylene thiuram tetrasulfide having a melting point of 112°C.; and tetramethyl thiuram tetrasulfide and any other solid water insoluble substituted thiuram polysulfides.

In the operation of the masterbatches of the present invention the accelerator is made of an aqueous slurry by either wetting the dry powder with sufficient water to completely wet the particles thereof or preferably making a slurry of the previously undried filter cake obtained from the preparation of the accelerator. When the undried filter cake is utilized, an exceedingly small particle size and superior dispersion may be obtained without necessity for a grinding or ball milling operation. Such a dispersion is more desirable than one obtained by using a slurry formed by simply wetting and pulverizing a previously dried accelerator although the latter may be used to prepare the slurry. The amount of water required in the slurry is not critical except that it is desirable that the particles be completely wetted so that they will be miscible with the latex without causing incipient coagulation, and a thin paste-like slurry is usually preferred. Examples of the latex utilized as a binding agent for the masterbatch are butadiene, isoprene, chloroprene, and the copolymers of one or more diolefinic compounds of less than 8 aliphatic carbon atoms with one or more copolymerizable monoolefines such as the hydrocarbon olefines, styrene and alpha methyl styrene, vinyl toluene, substituted olefines such as chlorinated styrenes, acrylo and methacrylonitriles, methyl methacrylate and other esters and

amides of acrylic and methacrylic acids, methyl-vinyl and methyl-isopropenyl ketones, vinyl pyridine and the like.

The proportion of rubber latex to accelerator in the masterbatch may vary widely as desired, the higher the percentage of rubber therein the easier the dispersion of the accelerator in the rubber mix without danger of local curing during the masticating process. It is generally uneconomical to use less than 25% of accelerator in the masterbatch composition and the benefits of dispersion and low concentration of masterbatches are decreased too greatly for most applications when the amount of the accelerator in the masterbatches is much greater than 75% of the weight of the masterbatch. In making the masterbatch the proportions of the latex and of the slurry are preferably selected so that the solids and the latices will be in the above percentage limits. All of the solids are considered to appear in the coagulum upon coagulation of the latex mixture.

The slurry of the accelerator and of the latex are thoroughly mixed and the mixture thereafter coagulated by any desirable method as, for example, by simply making the latex mixture unstable as by the addition thereto of electrolyte such as an acid and/or salt, for example aluminium sulfate, sodium chloride or acetic acid. By "acid" is meant a material which has a pH value of less than 7 in aqueous solution. Coagulation may also be accomplished without the use of these coagulating agents by simply drying the latex-vulcanizing agent mixture in a thin form section under a reduced pressure to remove water. By utilizing a relatively large amount of the accelerator having a small particle size, the surface area of the accelerator is sufficiently large to provide a coagulum in the form of a crumb which dries relatively easily and is exceptionally desirable from the standpoint of ease of dispersion when the masterbatch is added as a compounding agent in the preparation of rubber mixes. During drying it is exceptionally important that the temperature be maintained below the melting point and preferably below the softening point in the accelerator. In the case of the lower melting accelerators, the commercial drying operations are generally accomplished at reduced pressure and at a temperature which is only slightly elevated. Mastication of the coagulum, after drying has progressed to a considerable degree, is undesirable and is likely to cause vulcanizing contact of the rubber with the accelerator.

The following examples, in which parts are by weight, illustrate the present invention.

#### EXAMPLE 1

Wet filter cake of tetramethyl-thiuram disulfide (containing about 67% parts 130

solids and about 33% water). ... 300  
 Butadiene-styrene copolymer latex  
 (containing about 33% solids which  
 contain about 28% combined sty-  
 5 rene). ... 600  
 Water ... 400

The wet filter cake is mixed into the water to form a slurry and a slurry is then added with stirring to the above latex. After the latex and the slurry are thoroughly mixed, 200 parts of a 10% solution of sodium chloride is added to the above mixture with stirring and a 3% solution of sulfuric acid is stirred into the mixture a little at a time until 15 coagulation is complete. The coagulum is then separated from the liquid by filtering and the coagulum washed by spraying it with water while it is on the filter. The filtered product thus obtained is placed upon trays in a vacuum oven and heated to 80°C. under 20 reduced pressure, preferably about 100 mm of mercury or less, until drying of the coagulum is substantially complete. The coagulum thus obtained is packed in bags for 25 sale as a masterbatch.

A sample taken from the masterbatch above prepared was placed in a polyethylene bag and stored for one and one-half years at room temperature. When, after this elapsed 30 time, it was examined it showed no signs of any deterioration whatsoever. It dispersed very readily in rubber and had high acceleration activity.

#### EXAMPLE 2

35 The wet filter cake in the above Example 1 was substituted by 200 parts of pulverized tetramethyl thiuram disulfide. This material was then stirred into 500 parts of water containing 0.5% of wetting agent, such as an 40 alkyl aryl sulfonate, dissolved therein. The slurry was then mixed with GR-S type 20 latex in the same manner as was the slurry of Example 1. Other conditions remained substantially the same. The coagulum obtained after drying at a temperature well below 100°C. is easily dispersible in rubber and has exceptional storage ability. The 45 particle size of the masterbatch was somewhat larger in the case of Example 1 than in the case of Example 2. All or part of the tetramethyl thiuram disulfide in the above Example or any of the other water insoluble solid substituted thiuram disulfide accelerators may be substituted to provide master- 50 batches suitable for compounding into rubber mixes.

The tetramethyl thiuram disulfide is the preferred accelerating material, however. The latex used in the above Example may 60 be substituted by latices of other rubbery polymers of conjugated diolefinic compounds of less than 8 aliphatic carbon atoms, either natural or synthetic as above mentioned, rubber polymers being here considered as 65 those which are vulcanizable (of course after

suitable compounding) to a soft rubbery state.

In the above two Examples there is produced a masterbatch of solid substituted thiuram polysulfide accelerator which may 70 be stored for long periods of time without causing incipient vulcanization of the rubber thereof, even though the percentage of accelerator to rubber in the masterbatch is large.

Furthermore, the said two Examples, show 75 a method of making easily dispersible solid substituted thiuram polysulfide accelerator-rubbery polymer compositions suitable for incorporation into rubber compounds to provide vulcanization acceleration thereof 80 which easily dispersible compositions do not deteriorate upon relatively long storage such as one year or even more.

It is to be understood that variations and modifications of the specific invention here- 85 in shown and described may be made without going outside the scope of the invention.

What we claim is:—

1. A process of making a masterbatch of a curing type of accelerator, which com- 90 prises mixing a latex of a vulcanizable polymer or copolymer of a conjugated diolefinic compound of less than 8 aliphatic carbon atoms with an aqueous slurry of a solid water-insoluble substituted thiuram poly- 95 sulfide accelerator, coagulating the mixture thus formed, drying the coagulum while maintaining a temperature below the melting point of said substituted thiuram polysulfide and maintaining said coagulum in an 100 unmasticated condition.

2. A process according to Claim 1, wherein said substituted thiuram polysulfide is tetramethyl thiuram disulfide.

3. A process according to either of Claims 1 and 2, wherein the copolymer is a copoly- 105 mer of butadiene and styrene.

4. A vulcanization accelerator masterbatch for addition to a natural or synthetic rubber during the compounding of the same, 110 comprising an unmasticated, unvulcanized polymer or copolymer of a conjugated diolefinic compound of less than 8 aliphatic carbon atoms and at least one water insoluble solid substituted thiuram polysulfide 115 accelerator, said masterbatch being further characterized by being usable as a vulcanization accelerator after a period of storage of at least one month at normal temperatures.

5. An accelerator masterbatch according to Claim 4, comprising 25 to 75 parts by 120 weight of the polymer or copolymer and 75 to 25 parts by weight of the accelerator.

6. A masterbatch according to either of Claims 4 or 5 in crumb-like form. 125

7. A masterbatch according to any of Claims 4, 5 and 6 wherein said accelerator is tetramethyl thiuram disulfide.

8. A process of making a masterbatch of a curing type of accelerator substantially as 130

described herein with particular reference to any one of the Examples.

9. An accelerator masterbatch for addition to a rubber during the compounding of same substantially as described herein with par-

ticular reference to any one of the Examples.

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1. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

2. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

3. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

4. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

5. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

6. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

7. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

8. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

9. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

10. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

11. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

12. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

13. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

14. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

15. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

16. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

17. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

18. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

19. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.

20. A process for the preparation of a rubber composition comprising the steps of (a) compounding a rubber with an accelerator masterbatch substantially as described herein with particular reference to any one of the Examples, and (b) curing the resulting composition.